Case Study of Natural Attenuation of Trichloroethene at St. Joseph, Michigan

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1   Introduction

Trichloroethene (TCE) was found in the ground water at the St. Joseph Michigan Superfund site in 1982. The site is located four miles south of St. Joseph and one-half mile east of Lake Michigan. The site has been used for auto parts manufacturing since 1942. The aquifer is primarily composed of medium, fine and very fine glacial sands. The base of the aquifer is defined by a clay layer that lies between 21 and 29 meters below the ground surface. The elevation of the clay layer increases toward Lake Michigan. Investigation at the site included an exhaustive study of 41 possible contaminant sources, but did not definitively identify the source of the contamination. The source, however, was apparently situated over a ground water divide, as the contamination was divided into eastern and western plumes. Both plumes were found to contain trichloroethene (TCE), cis- and trans-1,2-dichloroethene (c-DCE and t-DCE), 1,1-dichloroethene (1,1-DCE) and vinyl chloride (VC). Initial investigation indicated that natural anaerobic degradation of the TCE was occurring in the western plume, because of the presence of transformation products and significant levels of ethene and methane [1], [3]. The purpose of this paper is to describe the investigation at the site and present the field evidence for natural attenuation of TCE. Since degradation of TCE is known to occur anaerobically under differing redox conditions and to produce specific daughter products, the relationships between measured concentrations of chlorinated ethenes and various redox indicators are emphasized below.

2   Sampling Strategy

Water samples were taken in October 1991 and March 1992 from a 5 foot-long slotted auger [5]. 17 boreholes were completed near the source of the western plume [1] that formed three transects that crossed the contaminant plume. Data from these first three transects has been analyzed by [4]. In 1992, two additional transects (4 and 5 on Figure 1) consisting of 9 additional slotted auger borings were completed. These two transects were chosen to sample the plume in the vicinity of Lake Michigan. In each boring, water samples were taken in 5 foot intervals from the water table to the base of the aquifer. On-site gas chromatography was used to determine the width of the plume and find the point of highest concentration in each transect. The on-site gas chromatography assured that the entire width of the contaminant plume had been captured within each transect. In August 1994, data were collected from a transect located about 100 m off-shore that was roughly parallel to the

shore line and contained 4 borings. Water samples were taken with a barge-mounted geoprobe [5]. Data from the lake transect showed the location of the plume by the observed reduction in dissolved oxygen concentration and the measured redox potentials.

3   Results

Figures 2 through 5 show the data from all the boreholes separated by transect, which in effect also separates them by sample date [1]. By compositing the data set, site wide trends can be seen. These figures are supplemented below by figures 6 through 9 showing the contaminant distribution with depth in single boreholes from representative locations. As shown in Figure 2, significant methane concentrations occurred where the dissolved oxygen concentration was low. Variation in concentration occurring on a scale smaller than the length of the auger is not accurately represented, as waters of differing chemistry may mix upon sampling. This may explain why there are a few data points that simultaneously have high methane and high oxygen concentration. Most importantly, the figure indicates that a large number of sample locations at the site had the necessary strong reducing conditions for reductive dechlorination to occur.

Figure 3 shows the distribution of sulfate and oxygen. Many of the points cluster near the sulfate axis which generally corresponds to the regions of high methane concentration. Generally the sulfate concentrations around the site are high and completely clear patterns of sulfate depletion are not found in the composited data set. The trends that exist in the data are best illustrated by the contaminant distribution in individual boreholes as described below. These data suggest that transformation of TCE to DCE occurred where the sulfate concentration showed some sign of decline. Figure 3 shows clustering of the sulfate data at sulfate concentration of 300 μM or less and oxygen concentration of 50 μM or lower.

As noted below many of these points occurred in the transition between the aerobic and methanogenic region. Compared with higher sulfate concentrations at many other locations, these points tentatively indicate sulfate reduction zones, which may be concurrent with methanogenesis (e.g., [2]). In particular, in transects 4 and 5 the uppermost sample locations were devoid of the contaminants and were oxygenated. Sulfate concentrations in the range of 300 μM to 500 μM at these points therefore indicate background sulfate levels.

The entire chlorinated ethene (TCE, the DCEs and VC) and ethene data set is plotted in Figure 4 as a chlorine number, N_{Cl}, that is defined by

$$N_{Cl} = \frac{\sum w_i C_i}{\sum C_i} \tag{1}$$

where w_i is the number of chlorine atoms in molecule i and C_i is the molar concentration of each ethene species. The chlorine number composites the ethene concentrations and scales them from 0 to 3. At zero no chlorinated species are present, and at 3 all of the ethene is in the form of TCE. Generally, the integer chlorine numbers (0,1,2,3) are obtained with nonzero concentration only of the ethene with that number of chlorine atoms. There are fortuitous combinations, however, of positive nonzero concentrations that give integer chloride numbers. None of these combinations occurred in the St. Joseph data set. Figure 4 shows that high chlorine numbers were associated with many of the high dissolved oxygen concentrations, indicating that most of the chlorine was contained in TCE molecules at these sampling points. Some of these had chlorine numbers of three indicating that

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[1] In each scatter plot (figures 2 through 5) the triangles represent data from transects 1, 2 and 3; the squares from transects 4 and 5; while the circles represent data from the lake transect

TCE was the only species present. The majority of locations with chlorine numbers below 3 were anaerobic which also corresponded to methanogenic locations. The latter condition, in conjunction with the presence of the TCE degradation products (indicated by the low chlorine numbers) indicates degradation of the TCE. When the data set is plotted against the methane concentration (figure 5), the data appeared scattered over most of the graph. The figure shows that some of the lowest chloride numbers were associated with the high methane concentrations. Generally, many of the down gradient locations (squares on Figure 3) showed chlorine numbers above 2 and lower methane concentration. These data suggest that in the down gradient transects TCE degraded to DCE under other than methanogenic conditions.

Data from selected borings are presented to represent the general trends with depth in each of the transects. In transect 2, located near the presumed source of contamination, dissolved oxygen was depleted below the 60 foot depth (figure 6). Between 45 feet and 60 feet, the 45 and 55 foot depths showed significant dissolved oxygen (figure 7, while they also showed significant methane concentration. Sulfate showed a weak declining trend with depth to about 70 feet. Significant TCE and cDCE concentrations were found only from 75 to 85 feet below the surface. Vinyl chloride was found at concentration of 40 μM or less over most of the borehole. Ethene was found at highest concentration at the bottom of the borehole, where the methane concentration also was highest.

Borehole T42 had the highest chlorinated ethene concentrations recorded for transect 4, and it also represents the general chemical distribution for the down gradient transects (figure 8). From the water table to the depth of 60 feet, oxygen concentrations were high but decreasing (figure 9). As noted above this contrasts to the up gradient transects which showed less consistent depletion of oxygen near the water table. Sulfate trended downward from 60 to 70 feet, roughly the same zone where oxygen was declining. From 70 to 85 feet the sulfate concentration remained low, but increased from 80 feet to the bottom of the borehole. Methane was not present in the aerobic zone above 65 feet, but it increased sharply in concentration from 70 to 80 feet before trending lower. Figure 8 shows the distribution of the chlorinated ethenes and ethene in T42. TCE was found from 60 feet downward with its maximum concentration occurring at the 70 foot depth. The region above the 60 foot depth was free from the chlorinated ethenes, so the high sulfate and oxygen concentrations there correspond to no activity due to degradation of the TCE. The cis DCE concentration was also highest at the 70 foot depth. Methane first appeared at 65 feet, and the peak cis DCE concentration occurred where sulfate concentration declined to its minimum. Vinyl chloride was found from 65 feet to the bottom of the borehole. Ethene was found from 70 feet downward, corresponding closely to the most methanogenic part of the borehole.

4   Conclusions

Because of a variety of evidence, the data set from St. Joseph suggested the occurrence of natural attenuation. The composited data set showed that, with the exception of a few points, the oxygenated and methanogenic zones of the aquifer were clearly separated. The presence of many methanogenic locations in the aquifer showed that required strongly reducing conditions for degradation of TCE existed in the aquifer. The distribution of the chloride number showed that the majority of sample locations where daughter products were present were also anaerobic. Data from individual boreholes indicated that high cDCE concentrations were commonly associated with declines in oxygen and sulfate concentration, and appeared upon the upper edge of the methanogenic zone. Generally, ethene was found in the most methanogenic portions of the aquifer and was also associated with relatively high vinyl chloride concentration, which indicates that the production of ethene was limited to those sample locations.

5 Disclaimer

This is an abstract of a proposed presentation and does not necessarily reflect EPA policy.

References

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[4] L. Semprini, P. K. Kitanidis, D. Kampbell, and J. T. Wilson. Anaerobic transformation of chlorinated aliphatic hydrocarbons in a sand aquifer based on spatial chemical distributions. *Water Resources Research*, 31(4):1051–1062, 1995.

[5] J. W. Weaver, J. T. Wilson, and D. H. Kampbell. Natural bioattenuation of trichloroethene at the St. Joseph, Michigan superfund site. Technical Report EPA/600/V-95/001, United States Environmental Protection Agency, 1995.
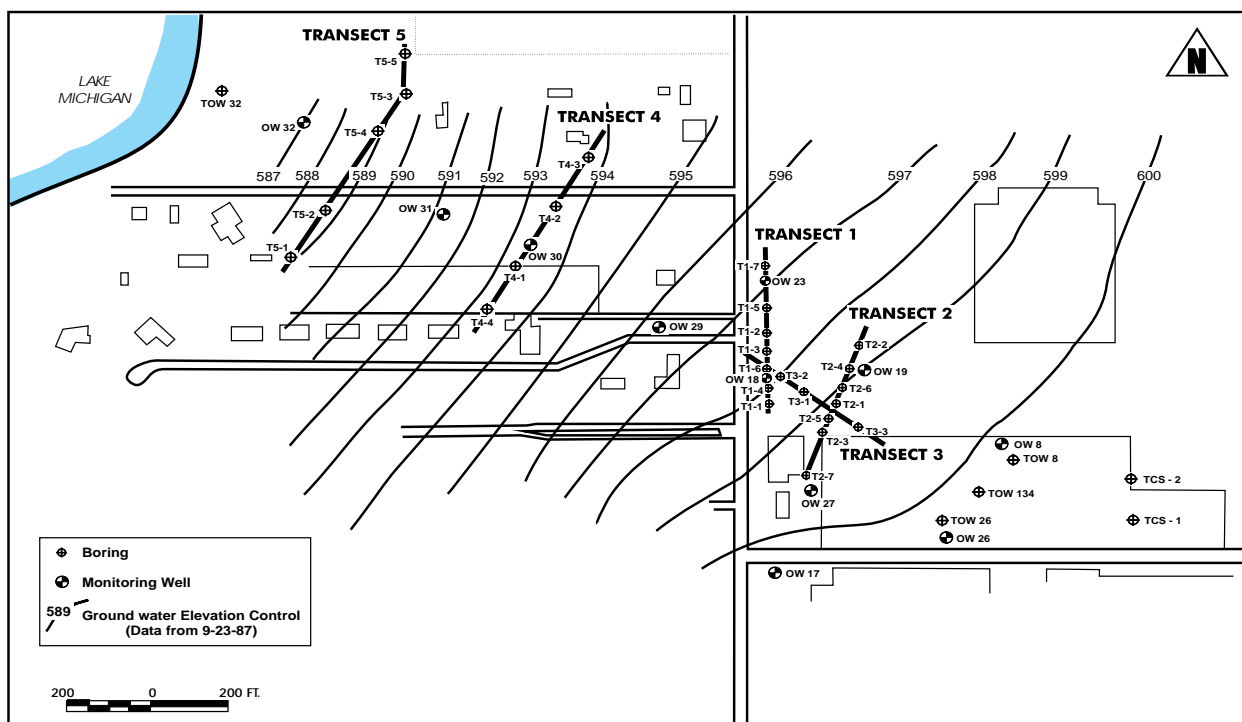
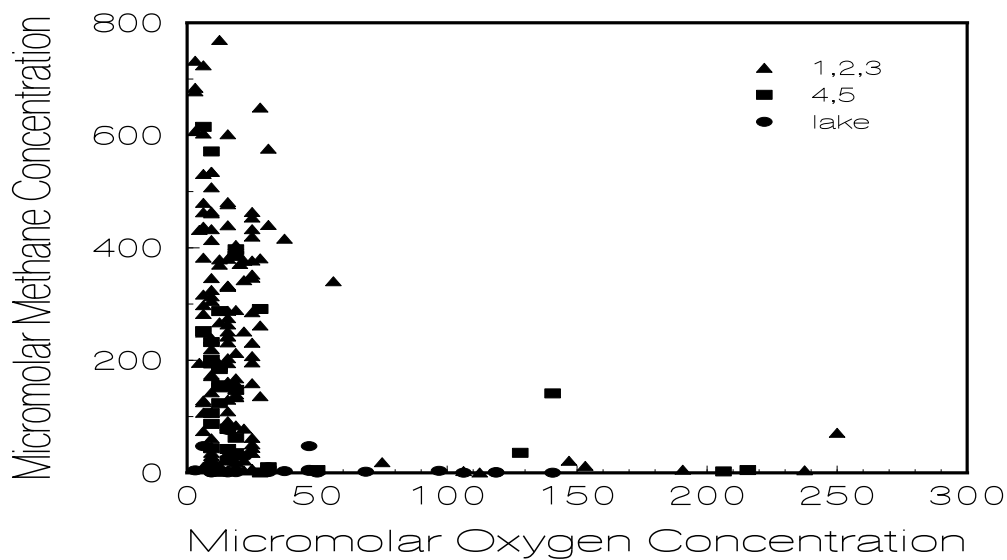Figure 1: St. Joseph superfund site plan
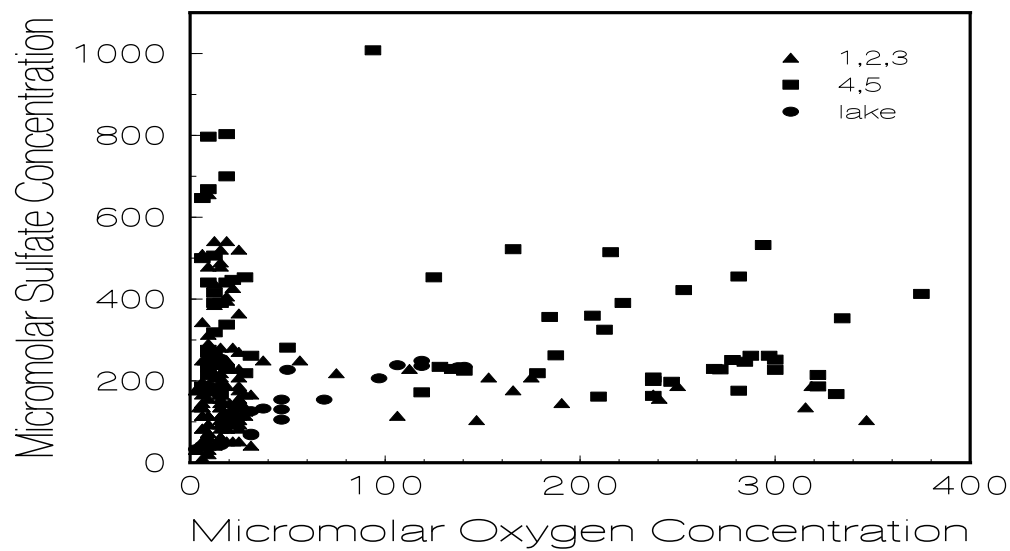

Figure 2: Scatter plot of methane and oxygen data

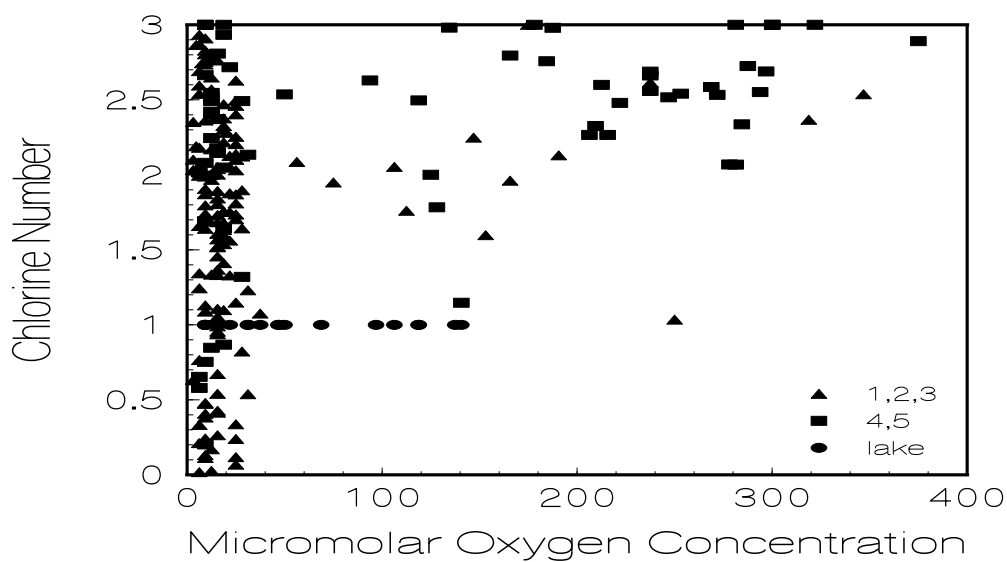Figure 3: Scatter plot of sulfate and oxygen data

Figure 4: Composited chlorine number plotted against oxygen concentration
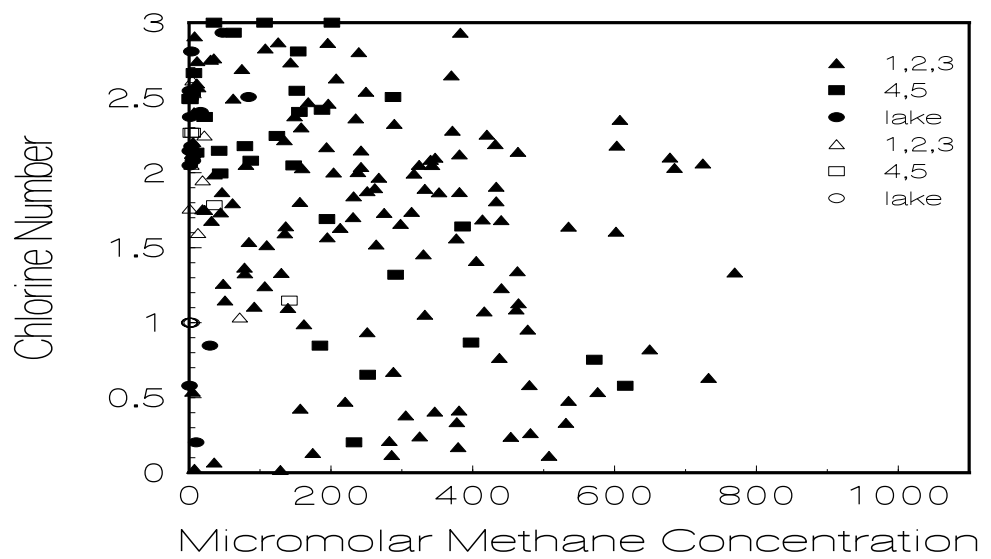
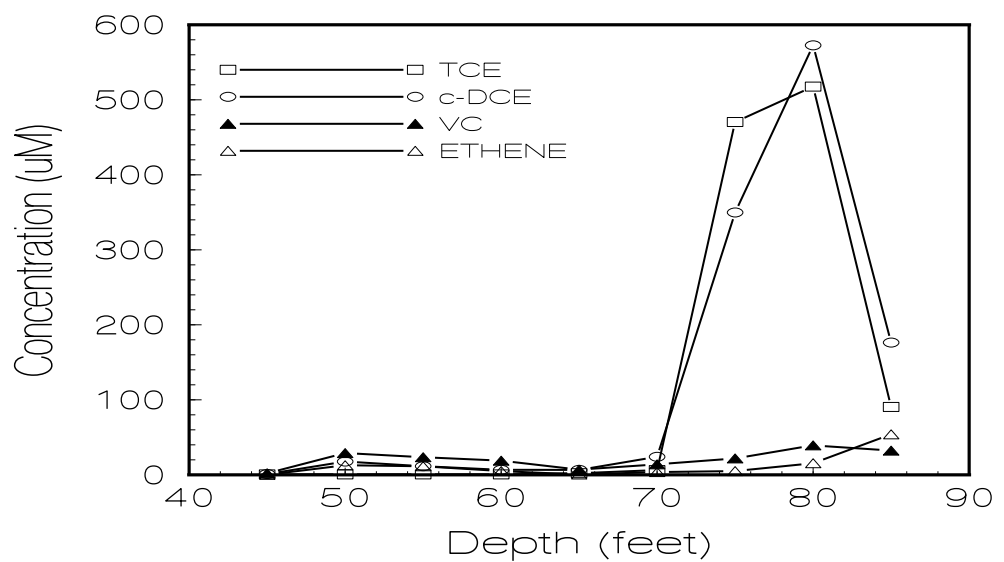Figure 5: Composited chlorine number plotted against methane concentration

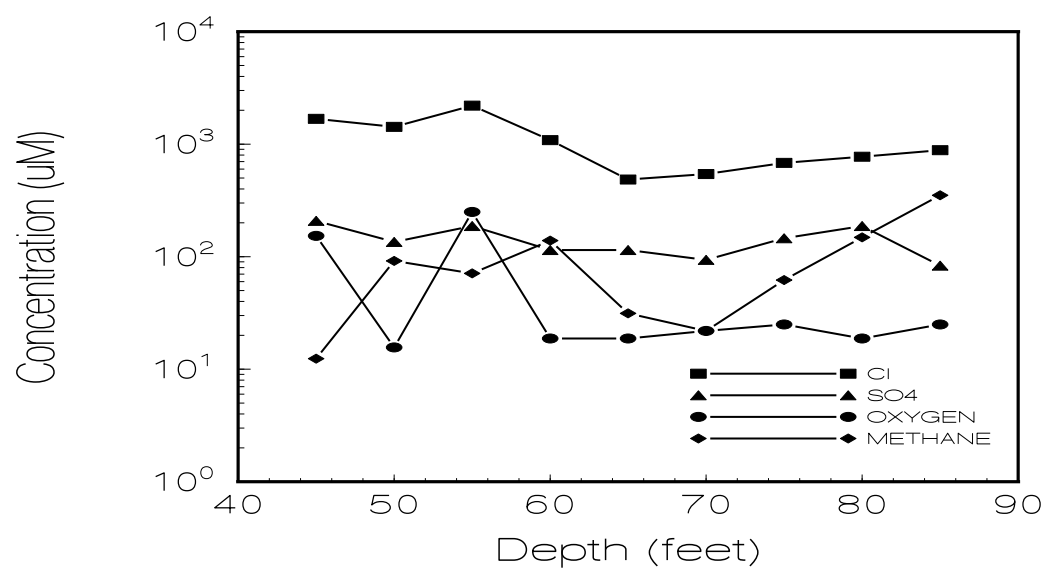Figure 6: Distribution of ethenes with depth at borehole T23

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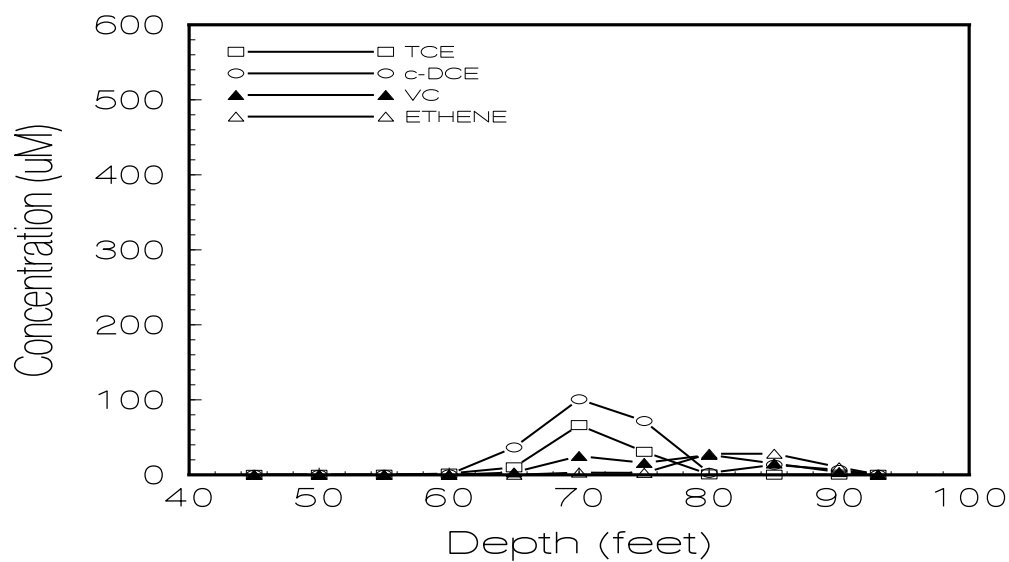Figure 7: Distribution of chloride, sulfate, dissolved oxygen and methane with depth in borehole T23

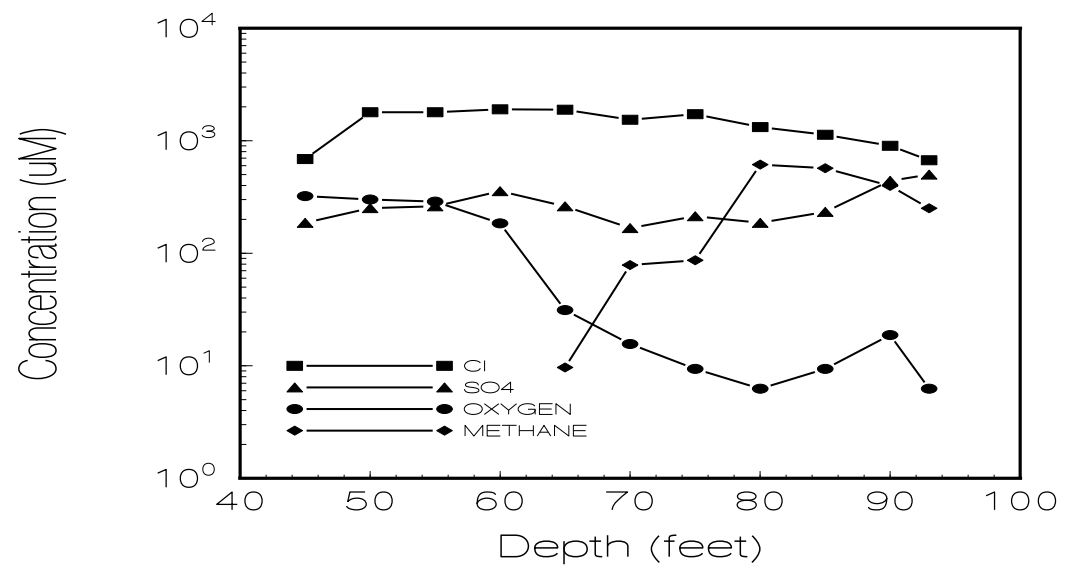Figure 8: Distribution of ethenes with depth in borehole T42

Figure 9: Distribution of chloride, sulfate, dissolved oxygen and methane with depth in borehole T42